

# Viscosity of Suspensions of Hard and Soft Spheres

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From a reanalysis of the published literature, the low-shear viscosity of suspensions of hard spheres is shown to have a dynamic crossover in its concentration dependence, from a stretched exponential at lower concentrations to a power law at elevated concentrations. The crossover is sharp, with no transition region in which neither form applies, and occurs at a volume fraction (ca. 0.41) and relative viscosity (ca. 11) well below the sphere volume fraction and relative viscosity (0.494, 49, respectively) of the lower phase boundary of the hard sphere melting transition. For soft spheres – taking many-arm star polymers as a model – with increasing sphere hardness  $\eta(\phi)$  shows a crossover from random-coil polymer behavior toward the behavior shown by true hard spheres.

## I. INTRODUCTION

An interesting theme in modern physics is the flow of granular preparations. While there is much interest in the flow of dry particulates (the ‘sandpile’ problem), an important issue in materials processing is the flow of solutions or suspensions of spherical or near-spherical particles. Solution flows are subject to rheological constraints, the simplest being the low-shear viscosity  $\eta$  of the solution.  $\eta$  depends very strongly on particle concentration. If an accurate functional form for the concentration dependence of  $\eta$  were available, one could predict  $\eta$  at an arbitrary concentration via interpolation from a small number of precise measurements.

Theoretical treatments of  $\eta$  of hard sphere suspensions at elevated  $\phi$  make a range of predictions. Jones, et al.[1] note results of Russell, et al.[2], but this treatment underestimates  $\eta$  for  $\phi > 0.4$ . de Schepper, et al.[3] show agreement between measurements of  $\eta$  and a theoretical treatment of de Schepper, et al.[4]. However, Ref. [4]’s treatment ignores solvent-mediated hydrodynamic interactions, so its relevance to the dynamics of a hard-sphere suspension is not transparent. Altenberger and Dahler[5] use the positive-function renormalization group[6] to extrapolate  $\eta$  from a low-concentration series, obtained from a hydrodynamic model, to elevated  $\phi$ . With reasonable values for input parameters, the Altenberger-Dahler calculation works well for  $\phi < 0.3$ , but gives an  $\eta$  that increases much too slowly with increasing volume fraction for  $\phi > 0.5$ .

It was recently demonstrated in a short note [7] for data[8, 9, 10] on polymethylmethacrylate spheres in *cis*-decalin and other organic solvents that the viscosity  $\eta$  of a hard sphere suspension has an accurate functional approximant. At lower ( $\phi < 0.42$ ) concentrations, one finds a stretched exponential

$$\eta(\phi) = \eta_o \exp(\alpha\phi^\nu), \quad (1)$$

while at higher ( $\phi > 0.42$ ) concentrations a power law

$$\eta(\phi) = \eta_1 \phi^x. \quad (2)$$

describes measurements well. Here  $\phi$  is the volume fraction of spheres,  $\alpha$  is a scaling prefactor,  $\nu$  and  $x$  are scaling exponents, and  $\eta_o$  and  $\eta_1$  are prefactors with units of viscosity. For hard spheres,  $\phi = 1.0$  is unattainable; for hard spheres  $\eta_1$  is therefore not the solution viscosity under physical circumstances. As seen in ref. [7], the transition between these two forms is sharp, with no significant crossover regime in which neither form is valid. This paper represents a substantial extension of the original note[7].

This paper explores the range of validity of eqs. 1 and 2. As shown below, these forms describe well the viscosity of a far wider range of systems and concentrations than reported in the preliminary note of ref. [7]. Particles considered here extend in size upwards from micelles or protein molecules, with concentrations ranging from near-dilute to the random packing limit. Some particles, such as silica nanospheres, are virtually incompressible; other particles are soft, permitting particle centers to approach to substantially less than twice the particle radius.

## II. BACKGROUND

Interpretation of experimental data on hard sphere suspensions arises in the first instance from equilibrium statistical mechanics. Close-packed hard spheres have a volume fraction  $\phi_{cp} > 0.7$ , but random close-packed systems generally attain volume fractions no greater than a nominal limit  $\phi_r \approx 0.64$ . Hoover and Ree[11] interpret their computer simulations as implying (1) suspensions of neutral hard spheres having  $\phi \leq \phi_m = 0.494$  are single (melt-like) phase fluids, (2) hard spheres having  $\phi \geq \phi_s = 0.55$  occupy an expanded solidlike phase, and (3) at intermediate volume fractions  $\phi_m \leq \phi \leq \phi_s$  the hard sphere system has an order-disorder transition, with an equilibrium between phases having volume fractions  $\phi_m$  and  $\phi_s$ . Hoover and Ree’s interpretation requires that equilibrium hard sphere suspensions with  $0.494 \leq \phi \leq 0.55$  are biphasic.

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The concentration-dependent low-shear viscosity  $\eta$  of hard sphere suspensions has been measured by a variety of authors, including Jones, et al.[1], Segre, et al.[8], Phan, et al.[9], Meeker, et al.[10], Cheng and Schachman[12], Marshall and Zukowski[13], van der Werff and de Kruiff[14], and de Kruif, et al.[15]. These references are not in precise numerical agreement, perhaps because at large  $\phi$  rheological properties are sensitive to small deviations of the suspended particles from perfect monodispersity and sphericity, and perhaps because small errors in determining  $\phi$  lead to a large scatter in measured values of  $\eta$  at a given nominal  $\phi$ . Most of these results involve  $\eta$  no more than a few hundred times the solvent viscosity  $\eta_s$ .

Phenomenologically, at low concentrations the zero-shear viscosity of a hard sphere suspension can be described by a pseudovirial approximant

$$\eta = \eta_s(1 + k_1\phi + k_2\phi^2 + k_3\phi^3 \dots) \quad (3)$$

where  $k_i$  are expansion coefficients. Cheng and Schachmann[12] confirmed the classic result  $k_1 = 2.5$  of Einstein for 260 nm diameter polystyrene spheres in 0.098 M NaCl. They were unable to determine  $k_2$  unequivocally.

The viscosity of a hard-sphere solution increases markedly with increasing sphere concentration. Data in refs. [8]-[10] refer only to the meltlike phase  $\phi \leq \phi_m$ , but other references attained higher concentrations. The recent and extremely thorough studies of Phan, et al.[9] and Meeker, et al.[10], both informed by the discussion between de Schepper, et al.[3] and Segre, et al.[16], find  $\eta = 45 \pm 3$  and  $\eta = 53 \pm 6$ , respectively, at volume fraction  $\phi_m = 0.494$ . Marshall and Zukowski[13] report  $\eta/\eta_s \approx 1 \cdot 10^8$  at  $\phi \approx 0.6$ .

Roovers[17] provides extensive data on the viscosity of a model soft-sphere system, namely solutions of many-armed polybutadiene star polymers whose effective hardness is modulated by changing the number of arms. The above references constitute a rheological phenomenology that can be compared with theoretical predictions.

Interesting, related results that go beyond the scope of this paper include studies on the frequency-dependent linear viscoelastic behavior of hard sphere suspensions by van der Werff, et al.[18] and on the rheology of zeroth-to-sixth generation dendrimers by Uppuluri, et al.[19]. At elevated concentrations, shear thinning sets in at high shear rates  $\dot{\gamma}$ . Marshall and Zukowski[13] report shear thinning for spheres of diameters 90, 210, and 286 nm above  $\phi \approx 0.2$ . Jones, et al.[1] record shear thinning for 50 nm spheres for  $\phi > 0.3$ . With 301 nm spheres, Segre, et al.[8] observe shear thinning above  $\phi \approx 0.4$ . There is thus no obvious correlation between sphere radius and the concentration for the onset of shear thinning, consistent with expectations for hard sphere systems. Marshall and Zukowski[13] report that for  $\phi > 0.5$  there is a marked increase in the characteristic time scale for shear thinning, while for  $\phi > 0.56$  at elevated  $\dot{\gamma}$  shear thinning is replaced by shear thickening. However, shear thicken-

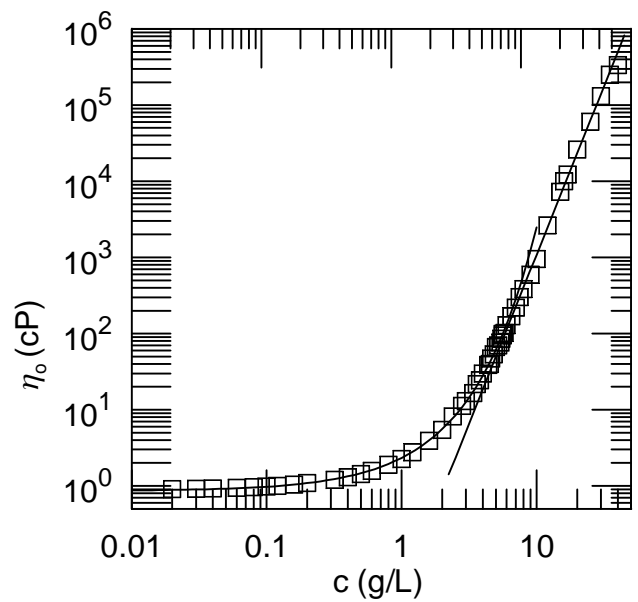


FIG. 1: Viscosity[20] of 1MDa hydroxypropylcellulose: water as a function of concentration, and fits to a low-concentration stretched exponential regime (smooth curve, eq 1) and a high-concentration power-law regime (straight line, eq 2).

ing was not observed by Jones et al.[1]. Jones, et al.[1] note that near the random-close-packed limiting concentration their systems gained a non-zero yield stress, with the elastic modulus satisfying  $G'(\omega) \sim \omega^0$  at higher volume fractions.

### III. RATIONALE

The conjectured form for the concentration dependence of  $\eta$  of a hard-sphere suspension, as successfully tested in ref. [7], arose from two sources. First, the form works empirically[20]-[24] to high precision in certain other complex fluids involving the same fundamental forces but having non-spherical particles. Second, an *ansatz* leading to the form and other results has been found on the basis of renormalization group concepts[25].

Representative empirical data providing a rationale for the conjecture, namely measurements of Quinlan, et al.[20] on  $\eta$  of high-molecular-weight hydroxypropylcellulose solutions, appear in Figure 1. The viscosity has a bifunctional concentration dependence, with two concentration regimes and a sharp crossover concentration. At low concentrations,  $\eta$  follows eq. 1, while at higher concentrations the power law of eq. 2 is followed. The crossover from stretched-exponential to power-law behavior occurs at a well-defined concentration  $\phi^+$ , with no indication near  $\phi^+$  of a crossover regime separating the stretched-exponential and power-law regimes.

This bifunctional concentration dependence of  $\eta$  is not

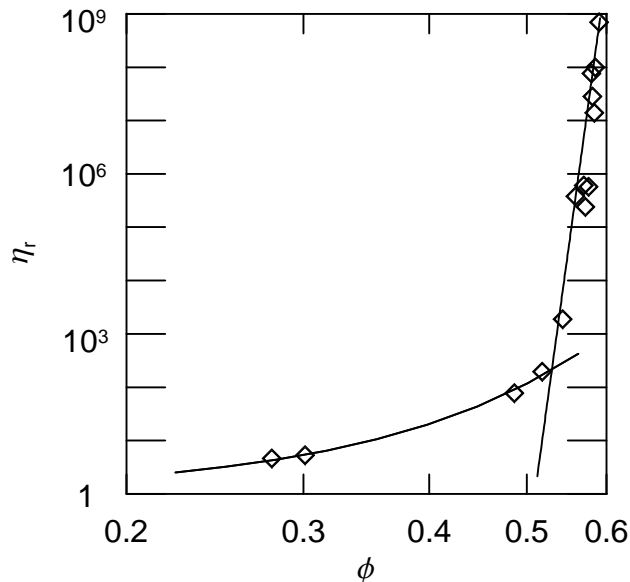


FIG. 2: Viscosity of 205 nm sterically stabilized silica spheres, after ref [13], and fits to eqs 1 (smooth curve) and 2 (straight line) using parameters in Table I.

unique to hydroxypropylcellulose solutions. Lin, et al.[21] had previously reported that  $\eta(\phi)$  in high-molecular-weight polyacrylic acid solutions had the same bifunctional concentration dependence. Similar transitions have since been identified[22, 23, 24] in data on some but not all solutions of high-molecular-weight polymers. The crossover concentration  $\phi^+$  is not a uniform multiple of the intrinsic viscosity  $[\eta]$ . In different systems,  $\phi^+$  variously appears[22, 23, 24] in the range  $4 \leq \phi^+[\eta] \leq 150$ , or not at all.

This author[25] has previously advanced a rationale for the observed concentration dependence of  $\eta$ . The rationale appears as part of a larger *ansatz* that correctly[25, 26] predicts the frequency dependence of the loss and storage moduli of a polymer solution over a full range of frequencies. Ref. [25] proposed that the concentration dependence of  $\eta$  out to high concentrations can be determined by applying the Altenberger-Dahler Positive Function Renormalization Group[5] method to the known lower-concentration series expansion for  $\eta$ . The functional form of  $\eta(\phi)$  is determined by the dominant fixed point of the renormalization group at each concentration  $\phi$ , leading automatically to a low-concentration stretched-exponential concentration dependence arising from a fixed point at  $\phi = 0$  and a possible power-law concentration dependence at larger concentrations corresponding to a large-concentration fixed point.

Polymer solutions are, of course, not identical to solutions of spherical colloids. However, the factor most likely to militate against the validity of the *ansatz* of ref. [25] for polymers is the hypothesized transition from

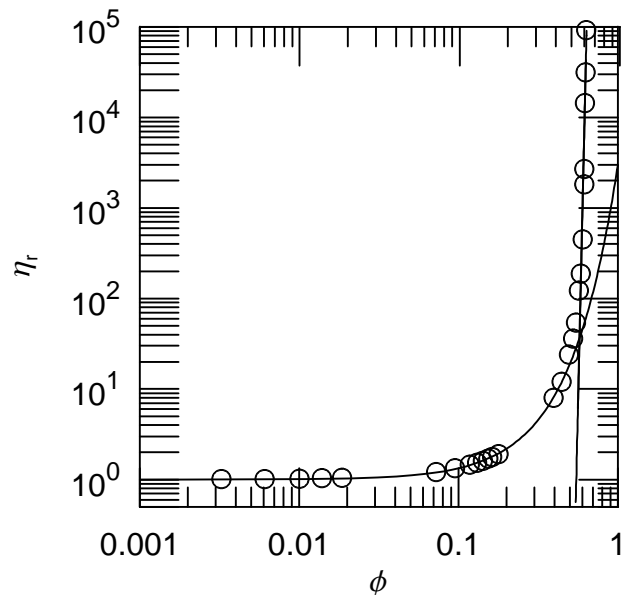


FIG. 3: Viscosity of 49 nm sterically stabilized silica spheres in Shellsol T, after ref [1]. Other details as in Fig 2.

hydrodynamic-dominated dynamics to entanglement-dominated dynamics. This transition might happen in polymer solutions, but suspended colloids cannot form entanglements. The apparent success of the *ansatz* in polymer solutions does not prove that the *ansatz* will succeed in colloid solutions, but the most obvious reason for a failure of the *ansatz* refers to polymer systems, where the *ansatz* appears to succeed.

#### IV. HARD SPHERE SUSPENSIONS

A literature search uncovered an extensive series of studies reported below. Functional fits to the reported data were made to eqs. 1 and 2 using non-linear least squares based on the simplex algorithm. Most papers actually reported the reduced viscosity  $\eta_r \equiv \eta/\eta_s$  rather than  $\eta$  directly, so  $\eta_o \approx 1$  often follows from fits to eq 1.

Marshall and Zukowski studied[13] sterically stabilized silica spheres, diameters 82, 205, and 288 nm suspended in decalin, using a Couette double concentric cylinder geometry for sphere volume fractions up to 0.592 and viscosities  $\eta/\eta_s$  up to almost  $10^9$ . Marshall and Zukowski's results on the 82 and 288 nm spheres were confined to the high-concentration power-law regime; the 288 nm data have a single point below the power-law regime. Figure 2 shows results on the 205 nm spheres, together with fits of the lower and upper concentration regions to eqs 1 and 2, respectively. Fitting parameters appear in Table I. The proposed concentration dependences are seen from the Figure to describe each region well. Because the power-law line is so steep, even very small experimental

errors in the concentrations lead to the large RMS fractional error reported for the fit.

Jones, et al.[1] measured the viscosity of 49-54 nm diameter silica spheres (different physical methods gave slightly different average diameters for the spheres) in Shellsol T (Shell Co.), using Ubbelohde capillary viscometers and three different cone and plate instruments for volume fractions up to 0.635 and relative viscosities as large as  $9.2 \times 10^4$ . Figure 3 presents their results and fits to our equations. As seen in Figure 3,  $\eta$  shows a stretched-exponential concentration dependence up to  $\phi \approx 0.45$  with a fractional RMS error of 1.3%, and a power-law concentration dependence for concentrations greater than approximately 0.55. In contrast to Figure 2, for  $0.45 \leq \phi \leq 0.55$  a transition regime is apparent in Figure 3: Several points do not quite lie on the lines describing the two functional forms.

A qualitative difference between Figs. 1 and 3—and thus between polymer chains and hard spheres—is seen in the relative position of the stretched-exponential and power-law curves. For a polymer solution (Figure 1) in the power-law regime the measured viscosities consistently lie below the viscosities predicted by extrapolating the stretched-exponential curve. For a sphere suspension (Figure 3) in the power-law regime the measured viscosities lie above the extrapolated stretched-exponential curve. In sphere suspensions,  $\eta$  thus increases smoothly until the crossover. Above the crossover the viscosity increases suddenly, far more steeply than expected from  $\eta(\phi)$  below the crossover. For polymers (Figure 1) the crossover between the stretched-exponential and power-law regimes is analytic (first derivative continuous). For hard spheres (Figure 3) the first derivative is not obviously continuous through the crossover.

van der Werff, et al[14] measured steady-shear viscosities of monodisperse silica dispersions of diameters 56, 94, 153, and ca. 230 nm in cyclohexane, using an Ubbelohde capillary viscometer as well as a rheometer with Couette and parallel-plate measuring cells. Figures 4a and 4b show their results for the smallest and largest spheres, together with the fitted curves. Table I includes fit parameters for all four sphere sizes. RMS fractional errors in the fits were 2-7% for the stretched exponential regime, and in most cases 8-9% for the power law regime. In Fig 4a, data points appear almost exactly at the intersection of the two curves. In these systems the crossover region between the two regimes, if any, must be extremely small.

DeKruif, et al.[15] measured shear stress against shear rate for 156 nm silica spheres in cyclohexane at volume fractions  $0.0006 \leq \phi \leq 0.6$  and viscosities  $\eta \leq 200\eta_s$ . Their measurements were confined almost entirely to the stretched-exponential regime. Fitting parameters appear in Table I.

Segre et al.[8] report the low-shear viscosity (obtained with a concentric-cylinder viscometer) and diffusion coefficient (from quasi-elastic light scattering) of 356 and 602 nm diameter polymethylmethacrylate spheres in *cis*-

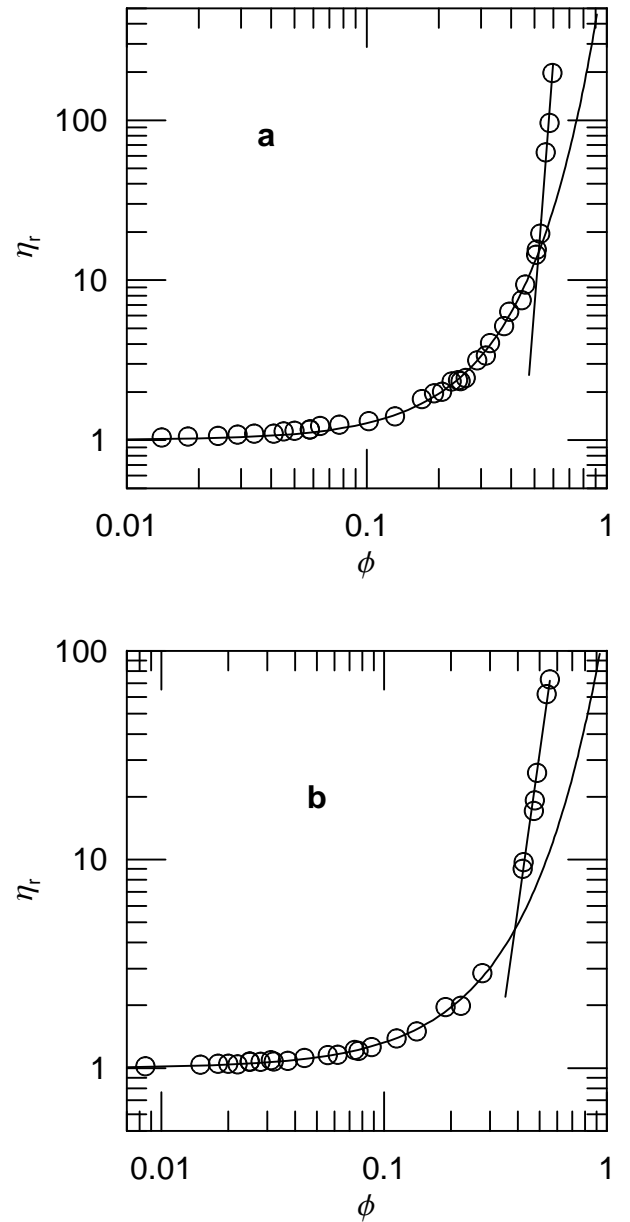


FIG. 4: Viscosity of (a) 56nm and (b) 230 nm sterically stabilized silica spheres in decalin, after ref [14]. Other details as in Fig 2.

decalin. Phan, et al.[9] and Meeker, et al.[10] studied  $\eta$  of 518 and 640 nm, and 602nm diameter, respectively, polymethylmethacrylate spheres in various solvents. These data have previously been analyzed in ref. [7]. Fitting parameters are included in Table I. These papers, which confined themselves to concentrations  $\phi \leq \phi_m$ , found distinct stretched-exponential and power law regimes, the transition occurring at  $0.41 \leq \phi^+ \leq 0.43$  and  $\eta_r \approx 10 - 15$ . The transition concentration  $\phi^+$  is substantially less than  $\phi_m$ . The differences between the sets of fitting parameters appears to reflect limits on measure-

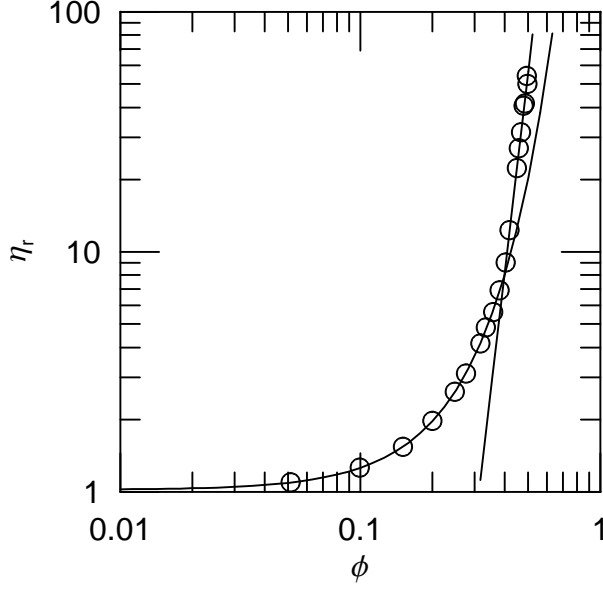


FIG. 5: Data of Segre, et al.[8] on sterically-stabilized 602 nm polymethylmethacrylate spheres in cis-decalin. Other details as in Fig 2.

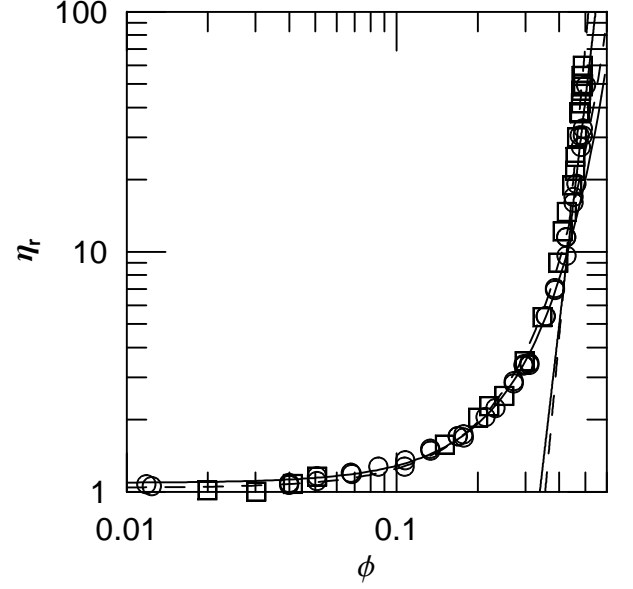


FIG. 6: Viscosity measurements of Phan, et al.[9] (circles, solid lines; 580 and 640 nm diameter) and Meeker, et al.[10] (squares, dashed lines; 602 nm diameter) on polymethylmethacrylate spheres in various solvents. Other details as in Fig 2.

ment accuracy.

## V. SOFT SPHERE SYSTEMS

The above results refer to spheres that are effectively non-deformable under the experimental conditions cited. A comparison with properties of deformable spheres is allowed by the data of Roovers[17] on solutions of 32-, 64-, 128-, and 270-arm polybutadiene star polymers. Roovers[17] determined viscosities with Cannon-Ubbelohde viscometers, using multiple size viscometers and very long flow times, e.g., 1-2 hours, to confirm the absence of shear thinning. Data were reported as a function of  $\phi/\phi^*$ , where  $\phi^*$  is the overlap concentration defined to be  $\phi^* = 0.4/[\eta]$ .

Roovers' stars had a variety of arm lengths and molecular weights  $0.4 \leq M \leq 11.2$  MDa. Figure 5 shows Roovers' data for ca. 3MDa stars; fit parameters appear in Table I. Fits were also made to data on stars of the other molecular weights. Roovers demonstrates that  $\eta$  at fixed reduced concentration and arm number is independent of star molecular weight. Correspondingly, when eqs 1 and 2, written as functions of  $\phi/\phi^*$ , are applied to Roovers' data, the resulting fit parameters are largely independent of molecular weight.

In Figure 5, arm number  $f$  increases from the lower-right-hand corner toward the upper-left-hand corner of the Figure. For  $\phi \leq 0.25\phi^*$ ,  $\eta$  is nearly independent of  $f$ . At any larger concentration,  $\eta$  of a 32-arm star is less than  $\eta$  of a 64-arm star, which is in turn less than  $\eta$  of a 128-

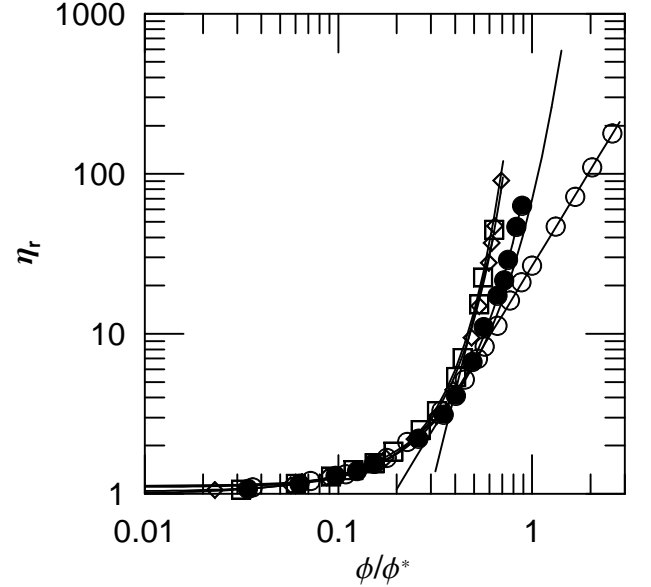


FIG. 7: Viscosity [17] of  $f$ -armed polybutadiene star polymers in toluene, for  $f$  of 32 ( $\circ$ ), 64 ( $\bullet$ ), 128 ( $\square$ ), and 270 ( $\diamond$ ), together with fits to eq 1 and (for the 32-arm stars) eq. 2. For the 32-arm stars the power-law curve falls under the stretched-exponential curve. For star polymers with  $f > 32$  the power-law curve would be superposed on the displayed stretched-exponential curves. For hard spheres, the power-law curve lies above the stretched-exponential curve, as seen in Figures 1-5.

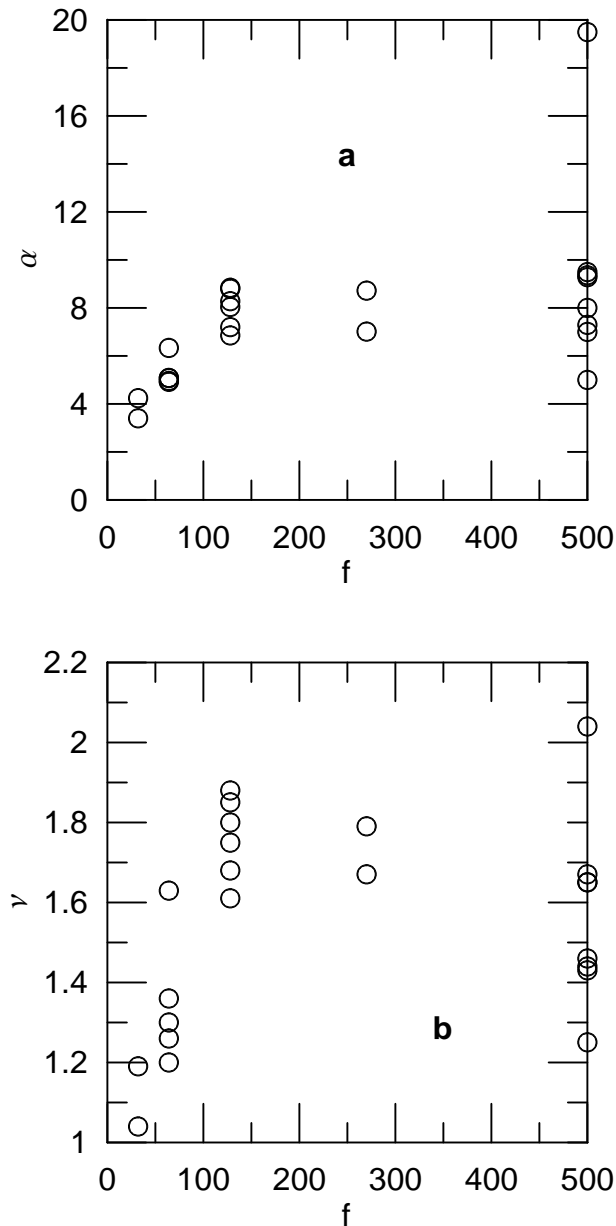


FIG. 8: a.  $\alpha$  and b.  $\nu$  as function of arm number  $f$ , based on fits to data of Roovers[17], with hard sphere results (Table I) plotted at  $f = 500$ , showing  $\eta(\phi)$  of 128- and 270-arm stars, as characterized by  $\alpha$  and  $\nu$ , has reached the asymptotic hard-sphere limit.

arm star. At fixed  $\phi/\phi^*$ , increasing the number of arms from 128 to 270 has no further effect on  $\eta$ , consistent with Roovers' interpretation that his materials have reached the limit of large  $f$ .

In the lower concentration regime,  $\alpha$  and  $\nu$  describe  $\eta(\phi)$ . Figures 6a and 6b show  $\alpha$  and  $\nu$  as functions of arm number. Points refer not only to the 3MDa stars of Fig. 5 but also to Roovers' other star polymers.  $\alpha$  and  $\nu$  for true hard spheres (Table I) are plotted in Fig. 6 as having

a nominal arm number  $f = 500$ . For  $f \leq 128$ ,  $\alpha$  and  $\nu$  both increase with increasing  $f$ ; for  $f \geq 128$ ,  $\alpha$  and  $\nu$  are both approximately independent of  $f$ . From Fig. 6, for  $\phi < \phi^+$  not only do  $f = 128$  and  $f = 270$  stars reach an asymptotic limit, but the limit is the hard-sphere limit.

$\eta$  of a 32-arm star shows a clear large- $\phi$  power-law regime, separated from the stretched-exponential regime via a crossover near  $\phi \approx 0.5$ . The crossover to this regime resembles that seen in Figure 1 for a polymer solution; the crossover is smooth and the measured  $\eta$  in the power-law regime is less than the  $\eta$  extrapolated to larger  $\phi$  from the stretched-exponential regime. If Roovers' 128- and 270-arm polymers had reached their hard-sphere limit in their viscometric properties, they would show a stretched-exponential to power-law transition near  $\phi/\phi^* \approx 0.4$ . Indeed, fits for these stars for  $\phi/\phi^* > 0.5$  to a power law obtain exponents  $x$  of 5.9 and 6.8. These exponents are slightly less than the exponents of 8-12 typical of true hard spheres, but are much larger than the  $x \approx 2$  found for 32-arm stars.

## VI. DISCUSSION

In the above, the published literature on  $\eta$  of solutions of hard spheres was re-examined. As seen in Table I, in almost all cases eqs 1 and 2 describe  $\eta(\phi)$  very well. In each set of data, a transition in the functional form of  $\eta$  is seen. For  $\phi < \phi^+$ , on a log-log plot  $\eta(\phi)$  is a smooth curve with a continuously varying slope. Above  $\phi^+$ , on the same log-log plot  $\eta(\phi)$  appears as a straight line of large and unvarying slope.

It has long been recognized that the viscosity of a hard-sphere suspension increases very sharply at elevated concentration. In prior discussions it was not always noted that there is a qualitative change in the form of  $\eta(\phi)$  when  $\eta$  begins its sharp increase. This apparent qualitative change in the functional form of  $\eta(\phi)$  explains the observations of Jones, et al.[1], Russell, et al.[2], and Altenberger and Dahler[5] that their low-volume-fraction forms for  $\eta(\phi)$  work for  $\phi < 0.3 - 0.4$ , but fail badly when  $\phi$  is taken to larger values.

Root-mean-square fractional errors in the fits are generally in the range 1- 9%. For hard spheres,  $\alpha$  is consistently in the range 7-11, while  $\nu$  is almost always between 1.4 and 1.8. The power-law exponent  $x$  is most often around 10. No pronounced dependence on any of these parameters on sphere radius is apparent, consistent with expectations that particle size should enter only through the sphere volume fraction  $\phi$ . Deviations from the proposed forms are seen in the high-concentration data of Marshall and Zukowski[13] and Jones et al[1], in that their data scatters very substantially around the power law form.

Table I reports the crossover concentrations  $\phi^+$  and crossover viscosities  $\eta^+$  at which the stretched-exponential and power-law forms intersect. In most systems,  $\phi^+$  is in the range 0.39-0.52, while  $4.6 \leq \eta_o^+ \leq 18.3$ .

TABLE I: Fitting Parameters for Rheological Data. Parameters from fits of  $\eta_o$  or  $\eta_o/\eta_s$  to eqs 1 and 2, root-mean-square fractional errors expressed as a percent (%R) in those fits, and crossover concentration  $\phi^+$  and crossover viscosity  $\eta^+$  between those forms. Note that  $\bar{\eta}$  represents the extended extrapolation of  $\eta(\phi)$  to  $\phi = 1$ ; even a modest error in the slope  $x$  leads to large errors in the estimated  $\bar{\eta}$ . For the data of ref [17], the first column gives the number of arms, not the diameter of the star.

Diameter	$\eta_s$	$\alpha$	$\nu$	%R	$\bar{\eta}$	$x$	%R	$\phi^+$	$\eta^+$
288 nm[13]	-	-	-	-	$4 \times 10^{13}$	37.1	70	-	-
205 nm[13]	1.0	19.5	2.04	12	$9.5 \times 10^7$	10	78	0.53	206
49 nm [1]	1	8.0	1.44	1.3	$1 \times 10^{20}$	77	46	0.58	37.1
56 nm [14]	1	7.0	1.46	5	$4.7 \times 10^6$	19.4	8	0.52	14.8
94 nm [14]	1	9.5	1.67	7	$1.7 \times 10^4$	8.97	18	0.44	11.5
153 nm [14]	1	7.3	1.43	4	$3.2 \times 10^3$	12.1	8	0.48	12.6
230 nm [14]	1	5	1.25	2	$6.1 \times 10^3$	7.57	9	0.39	4.6
152 nm [15]	1	9.27	1.65	6.4	$6.1 \times 10^8$	12.4	2.0	0.49	18.3
302nm [8]	1.02	9.35	1.65	0.9	$7.5 \times 10^6$	8.52	3.6	0.40	7.9
518 & 640nm [9]	1.09	9.98	1.78	3.6	$3.0 \times 10^4$	9.46	8.2	0.42	10
602nm [10]	1.04	11.1	1.78	4.3	$3.9 \times 10^5$	12.5	8.2	0.42	12
$f = 32$ [17]	0.99	4.24	1.19	1.8	19.5	1.96	1.0	-	-
$f = 64$ [17]	1.03	4.91	1.36	4.5	68.2	3.9	9.2	-	-
$f = 128$ [17]	1.12	8.28	1.80	4.9	644	5.9	4.8	-	-
$f = 270$ [17]	1.09	7.01	1.67	3.8	1030	6.8	7.4	-	-

The transition in the concentration dependence of  $\eta$  is not a dynamic simply reflection of the equilibrium phase boundary at  $\phi_m$ . Phan, et al.[9] and Meeker, et al.[10] did precise measurements of  $\eta(\phi)$  up to  $\phi_m$ . On analysis, their data shows that the dynamic transition occurs at  $\phi^+ \approx 0.42$ ,  $\eta^+ \approx 10 - 12$ . Thus,  $\phi^+$  is well below the carefully determined  $\phi_m = 0.494$ , at which concentration  $\eta \approx 49$ , well above  $\eta^+$  that we have determined. In almost all systems  $\eta^+$  is in the range 8-18, well below the experimental  $\eta(\phi_m)$ .

While a systematic error in determining  $\phi$  affects the determination of  $\phi^+$ , it has no effect on  $\eta^+$ . Disagreements between determinations of  $\eta^+$  thus cannot be related to difficulties in determining  $\phi$ . An alternative plausible explanation for the experimental variation in  $\eta^+$  is that the crossover is sensitive to details of the interparticle potential, so that varying degrees of sphere polydispersity or non-sphericity affect the crossover's location.

Several physical explanations for the apparent dynamic crossover suggest themselves:

1) The crossover might arise from a change in the static correlations in the system. While it appears that  $\phi^+$  is less than the lower melting concentration  $\phi_m$ , dynamic effects are typically more sensitive to three-body correlations than are static correlations. One cannot readily exclude the possibility that there are significant changes in  $g^{(3)}(\mathbf{r}_1, \mathbf{r}_2, \mathbf{r}_3)$  of hard spheres, as a precursor to the transition at  $\phi = \phi_m$ , at some concentration such as  $\phi^+$  that lies below  $\phi_m$ .

2) The crossover might result from additional dynamic correlations in the system at elevated  $\phi$ . The oft-discussed formation of sphere doublets in shear at large  $\phi$  would have this effect. Such doublets could play the

same qualitative role in sphere viscosity that is played in some treatments of polymer viscosity by the transient tube of the reptation model. The doublets and the tube walls only appear at high concentration; each serves to obstruct lateral motion of the translating species.

3) The crossover might be a purely mathematical consequence of taking low-concentration interactions to high concentration. Altenberger and Dahler[5, 6] have shown how a renormalization-group method can be used to calculate  $\eta$  at elevated  $\phi$ . Renormalization group methods involve series expansions around fixed points. If a full renormalization group treatment of  $\eta(\phi)$  were appropriate and if it had fixed points at  $\phi = 0$  and also at elevated  $\phi$ , then there would be a transition concentration at which one dominant fixed point replaces the other, for purely mathematical reasons. Associated with this change in the identity of the fixed point would be a change in the functional dependence of  $\eta$  on  $\phi$ .

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